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Inorganic Linkage Isomerism of the Thiocyanate Ion

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Linkage isomers of metal complexes of the type M–SCN (thiocyanato) and M–NCS (isothiocyanato) are reported for the compounds $[\mathrm{Pd(As(C_6H_5)_3)_2X_2}]$ and $[\mathrm{Pd(bipy)X_2}]$. The method of preparation depends on the rapid isolation of the kinetic reaction product prior to its rearrangement to the stable form. It is suggested that both electronic and steric factors of the coordinated ligands contribute to the nature of $\mathrm{SCN^-}$ bonding in complexes of Pd(II) and Pt(II).

Introduction

This study was concerned with what is the least familiar of the types of isomerism found in coordination chemistry, namely, linkage isomerism. Linkage isomerism occurs whenever a given ligand can attach itself to the same central metal atom by bonding through either one of two different atoms within the ligand. For true linkage isomerism, all other factors, such as the geometrical configuration, just remain the same.

Prior to this work, the only ligand known to exhibit this type of isomerism in metal complexes was the nitrile ion, $\mathrm{NO_2^-}$. The first example was reported in 1893 by Jørgensen,[2] who isolated the nitro (Co–$\mathrm{NO_2}$) and nitrito (Co–ONO) pentaammines of cobalt(III). Recently, Basolo and Hammaker[3] succeeded in extending nitro–nitrito linkage isomerism to include the pentaammines of rhodium(III), iridium(III), and platinum(IV).

The thiocyanate ion, $:\mathrm{N}{\equiv}\mathrm{C}{-}\underset{\cdot\cdot}{\ddot{\mathrm{S}}}:^-$, presents itself as the most logical candidate for a second example of linkage isomerism. It is known to form both thiocyanato (M–SCN) and isothiocyanato (M–NCS) complexes, depending on the central metal atom employed,[4] as well as bridged (M–SCN–M) species.[5] Several authors[6,7] have pointed out that the change from M–NCS to M–SCN bonding coincides approximately in the periodic table with the change in the relative bonding strengths of the halide ions from $\mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$ to $\mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{F^-}$. The first order is followed by halogeno complexes of metals of the first transition series, the second order by halogeno complexes of metals to the right of group VII in the second and third transition series, the class a and class b acceptors, respectively, proposed by Ahrland, Chatt, and Davies[8] for the coordination of metal ions with an extensive series of ligands. Several explanations have been proposed for this change.[8,9] The most recent, by Pearson,[9c] suggests that S in $\mathrm{SCN^-}$ is soft and will prefer to coordinate with soft acids (class b metals) whereas N in $\mathrm{SCN^-}$ is hard and coordinates with hard acids (class a metals). The terms soft and hard are used to designate substances which are polarizable and nonpolarizable, respectively. The generalization of thiocyanate bonding given above applies only to complexes wherein thiocyanate is the sole ligand.

The only previously reported attempt to prepare inorganic linkage isomers of the thiocyanate ion was for chromium(III) complexes[10] and was not successful. The initial attempts to prepare thiocyanate linkage isomers in our study were formulated along the same lines and were also unsuccessful.

Success was finally realized, due largely to an interesting and significant observation made by Turco and Pecile.[11] They found that, for palladium(II) and platinum(II) complexes, coordinated thiocyanate ion is either S- or N-bonded, depending upon the nature of the other ligands present. Thus, the systems $[\mathrm{M(SCN)_4}]^{2-}$ and $[\mathrm{M(NH_3)_2(SCN)_2}]$ are S-bonded, whereas $[\mathrm{M(PR_3)_2(NCS)_2}]$ is N-bonded. It follows that, in these systems, there should be some borderline ligands for which the energy difference between the M–SCN and M–NCS isomers is relatively small, permitting isolation of both. This paper reports the effects of a series of ligands on thiocyanate bonding in palladium(II) and platinum(II) complexes, and the synthesis,[12] characterization, and preliminary kinetics of the isomerization of thiocyanato and isothiocyanato isomers of some palladium(II) complexes.

Experimental

Preparation of Complexes.—Most of the complexes were prepared by essentially the same method. This involved mixing an aqueous solution of $\mathrm{K_2[MX_4]}$, where M is Pd(II) or Pt(II) and $\mathrm{X^-}$ is $\mathrm{SCN^-}$ or $\mathrm{Cl^-}$, with an alcoholic solution of a stoichiometric amount of a monodentate ligand, L, or a bidentate ligand, L′, to give the corresponding products $[\mathrm{ML_2X_2}]$ or $[\mathrm{ML'X_2}]$. Aqueous solutions of L were used in the preparations of the pyridine and

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TABLE I

STIRRING PERIODS, PER CENT YIELDS, AND ANALYTICAL DATA FOR THE $[ML_2X_2]$ AND $[ML'X_2]$ COMPLEXES

			Analyses, %					
			Theory			Found		
Complex[a]	Stirring period, hr.	Yield, %	C	H	N	C	H	N
$[Pd(P(n\text{-}C_4H_9)_3)_2(NCS)_2]$	1.25[b]	31.2	49.79	8.68	4.47	49.50	8.23	4.74
$[Pd(P(C_6H_5)_3)_2Cl_2]$	0.05[c]	82.4	61.60	4.31		62.72	4.41	
$[Pd(P(C_6H_5)_3)_2(NCS)_2]$	3.0[c]	94.3	61.07	4.05	3.75	61.29	4.20	3.59
$[Pd(As(n\text{-}C_4H_9)_3)_2Cl_2]$	0.02[b]	Not det.	43.03	8.13		42.87	8.04	
$[Pd(As(n\text{-}C_4H_9)_3)_2(NCS)_2]$	0.12[b]	Not det.	43.67	7.61	3.92	45.10	7.53	2.92
$[Pd(As(C_6H_5)_3)_2Cl_2]$	0.08[c]	85.1	54.75	3.83		54.79	3.91	
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	3.0[c]	85.0	54.66	3.62	3.36	54.63	3.65	3.44
$[Pd(Sb(C_6H_5)_3)_2Cl_2]$	0.08[c]	58.9	48.95	3.42		48.89	3.26	
$[Pd(Sb(C_6H_5)_3)_2(SCN)_2]$	3.0[c]	12.8	49.15	3.26	3.02	49.54	3.30	2.99
$[Pd(py)_2Cl_2]$	0.08[b]	70.4	35.80	3.00		35.83	2.93	
$[Pd(py)_2(NCS)_2]$	0.17[b]	66.8	37.84	2.65	14.71	37.31	2.73	14.59
$[Pd(\gamma\text{-pic})_2Cl_2]$	0.08[b]	72.8	39.65	3.88		39.74	4.03	
$[Pd(\gamma\text{-pic})_2(SCN)_2]$	0.33[b]	81.2	41.15	3.45	13.71	41.39	3.57	13.43
$[Pd(4\text{-}n\text{-ampy})_2Cl_2]$	0.08[b]	Not det.	50.49	6.36		50.36	6.34	
$[Pd(4\text{-}n\text{-ampy})_2(SCN)_2]$	0.07[b]	Not det.	50.71	5.80	10.75	51.96	5.89	10.62
$[Pd(bipy)Cl_2]$	0.50[b]	96.5	36.02	2.42		35.96	2.63	
$[Pd(bipy)(NCS)_2]$	0.17[b]	94.0	38.04	2.13	14.79	38.01	2.34	14.86
$[Pd(phen)Cl_2]$	0.05[b]	Not det.	40.31	2.26		40.49	2.32	
$[Pd(phen)(SCN)_2]$	0.05[b]	Not det.	41.76	2.00	13.91	41.79	2.17	13.75
$[Pd(tu)_2(SCN)_2]$	24.0[c]	Not det.	12.82	2.15	22.43	12.96	2.07	22.58
$[Pd(etu)_2Cl_2]$	34.5[c]	Not det.	18.87	3.17		18.44	3.27	
$[Pd(etu)_2(SCN)_2]$	1.0[c]	Not det.	22.51	2.83	19.69	23.23	2.95	19.33
$[Pt(P(C_6H_5)_3)_2Cl_2]$	3.5[c]	98.0	54.69	3.83		55.07	3.36	
$[Pt(P(C_6H_5)_3)_2(NCS)_2]$	2.5[c]	93.0	54.60	3.62	3.35	53.16	3.66	3.27
$[Pt(As(C_6H_5)_3)_2(NCS)_2]$	1.0[c]	67.8	49.41	3.27	3.03	49.34	3.31	3.12
$[Pt(Sb(C_6H_5)_3)_2Cl_2]$	4.0[c]	69.1	44.48	3.11		44.56	3.10	
$[Pt(Sb(C_6H_5)_3)_2(SCN)_2]$	2.0[c]	49.0	44.86	2.97	2.75	44.69	2.99	2.79
$[Pt(py)_2Cl_2]$	6.5[b]	81.8	28.31	2.38		28.60	2.36	
$[Pt(py)_2(NCS)_2]$	0.5[b]	75.4	30.70	2.15	11.94	30.58	2.30	11.76
$[Pt(bipy)(NCS)_2]$	24.0[b]	<1	30.83	1.73	11.99	30.36	1.95	11.52

[a] Some of the compounds reported here had previously been prepared and are described in the literature. [b] Both reactant solutions were at room temperature before being mixed. [c] A room temperature solution of $K_2[MX_4]$ was mixed with an ~75° ethanolic solution of the stoichiometric amount of ligand. Abbreviations: py, pyridine; bipy, 2,2'-bipyridine; γ-pic, γ-picoline (4-methylpyridine); 4-*n*-ampy, 4-*n*-amylpyridine; phen, 1,10-phenanthroline; tu, thiourea; etu, ethylenethiourea. Whenever the symbol NCS^- is written in a compound this designates M–NCS bonding, whereas SCN^- designates M–SCN bonding.

4-methylpyridine complexes. The amounts used were of the order of 1 mmole of $K_2[MX_4]$, dissolved in 5 ml. of H_2O, and 2 mmoles of L or 1 mmole of L', dissolved in 5 ml. of absolute C_2H_5OH. After stirring the reaction mixture with a magnetic stirrer for a period of time to allow for the completion of the reaction, the product was isolated by vacuum filtration, washed with H_2O, absolute C_2H_5OH, and ethyl ether, and dried *in vacuo* over P_2O_5. The products precipitated from solution immediately upon their formation. The rates of the reactions varied, those involving Pd(II) being essentially instantaneous, those involving Pt(II) being much slower. Usually, both reactant solutions were mixed at room temperature. In some cases, the relatively low solubility of the ligand in absolute C_2H_5OH necessitated the use of an ethanolic ligand solution whose temperature was close to the boiling point of C_2H_5OH. The stirring periods employed, per cent yields obtained, and analyses of the complexes prepared by the foregoing method are shown in Table I.

No attempt was made to ascertain the structures of these compounds beyond the determination of the bonding involved (M–SCN or M–NCS) in the thiocyanate-containing complexes. It is reasonable to assume that they are square-planar complexes. Furthermore, the Pd(II) complexes all probably have the *trans* configuration, except, of course, the complexes containing 2,2'-bipyridine and 1,10-phenanthroline. It was noted by Mann and Purdie,[13] who prepared a series of compounds of the general formula $[Pd(LR_3)_2X_2]$, where L is either P or As, R is an alkyl group, and X^- is Cl^-, Br^-, or I^-, that with the exception of the $As(CH_3)_3$ derivative, only the *trans* isomer could be made. The Pt(II) complexes probably have the *cis* configuration.[14]

Compounds which were not prepared by the above general method and which are not listed in Table I are discussed here separately.

cis- **and** *trans*-**$[Pt(As(C_6H_5)_3)_2Cl_2]$**.—These geometric isomers were prepared according to the method of Jensen.[14]

Anal. Calcd. for $PtAs_2C_{36}H_{30}Cl_2$: Pt, 22.21. Found, for the *cis* isomer: Pt, 22.1; for the *trans* isomer; Pt, 22.5.

$[Pt(bipy)Cl_2]$ and $[Pt(bipy)_2][PtCl_4]$.—These compounds were prepared according to the methods of Morgan and Burstall.[15]

Anal. Calcd. for $PtCl_{10}H_8N_2Cl_2$ and $Pt_2C_{20}H_{16}N_4Cl_4$: C, 28.45; H, 1.91; Pt, 46.30. Found, for $[Pt(bipy)Cl_2]$: Pt, 46.2; for $[Pt(bipy)_2][PtCl_4]$: C, 28.08; H, 2.59.

$[Pt(bipy)_2][Pt(SCN)_4]$ was prepared in a completely analogous manner. The analytical results, however, were poor for the brick-red solid obtained.

Anal. Calcd. for $Pt_2C_{24}H_{16}N_8S_4$: C, 30.83; H, 1.73; N, 11.99; Pt, 41.74. Found: C, 29.56; H, 2.01; N, 10.20; Pt, 41.9.

cis-**$[Pt(NH_3)_2(SCN)_2]$**.—To a solution of 0.89 g. (5.2 mmoles) of $AgNO_3$ in 5 ml. of H_2O was added 0.78 g. (2.6 mmoles) of *cis*-$[Pt(NH_3)_2Cl_2]$. The mixture was heated on a steam bath until the only solid remaining was a pure white precipitate of AgCl. The AgCl was removed by filtration and the filtrate placed in an ice bath. To the filtrate was added 0.89 g. (5.2 mmoles) of KSCN, dissolved in 2 ml. of H_2O, resulting in the precipitation of a bright yellow solid, which was collected, washed with H_2O, C_2H_5OH, and $(C_2H_5)_2O$, and dried *in vacuo* over P_2O_5.

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Anal. Calcd. for $PtC_2H_6N_4S_2$: C, 6.96; H, 1.75; N, 16.23. Found: C, 6.89; H, 1.51; N, 15.97.

trans-**[Pt(NH$_3$)$_2$(SCN)$_2$]**, pale yellow in color, was prepared in the same manner, starting with *trans*-[Pt(NH$_3$)$_2$Cl$_2$].

Anal. Found: C, 7.14; H, 1.73; N, 16.18.

[Pd(bipy)$_2$](B(C$_6$H$_5$)$_4$)$_2$.—A mixture of 0.22 g. (0.7 mmole) of [Pd(bipy)Cl$_2$] and 0.22 g. (1.4 mmoles) of 2,2′-bipyridine in H_2O was heated on a steam bath until the [Pd(bipy)Cl$_2$] dissolved, due to the formation of $[Pd(bipy)_2]^{2+}$. The solution was cooled in an ice–salt bath and passed through a filter. To the filtrate was added a solution of 0.51 g. (1.5 mmoles) of Na[B(C$_6$H$_5$)$_4$] in 25 ml. of H_2O. A light yellow precipitate formed immediately. This was collected on a filter and dried *in vacuo* over Mg(ClO$_4$)$_2$.

Anal. Calcd. for $PdC_{44}H_{36}N_4B$: C, 77.25; H, 5.34. Found: C, 78.53; H, 5.56.

[Pd(bipy)$_2$](ClO$_4$)$_2$ was prepared in a similar fashion, using $Ba(ClO_4)_2 \cdot 2H_2O$ as the precipitating agent.[16] Analysis by combustion was not attempted because such perchlorates explode when heated.

[Pd(bipy)$_2$][PdCl$_4$].—[Pd(bipy)$_2$](ClO$_4$)$_2$ (0.18 g., 0.3 mmole) and K$_2$[PdCl$_4$] (0.10 g., 0.3 mmole) were stirred in 20 ml. of H_2O for 45 min. Filtration yielded a pink solid which was dried *in vacuo* over Mg(ClO$_4$)$_2$. The product contained some entrapped [Pd(bipy)$_2$](ClO$_4$)$_2$, as determined from the infrared spectrum of the product.

[Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$].—K$_2$Pd(SCN)$_4$ (1.03 g., 2.47 mmoles), dissolved in 25 ml. of absolute C_2H_5OH and 5 drops of H_2O, and As(C$_6$H$_5$)$_3$ (1.52 g., 4.95 mmoles), dissolved in 25 ml. of absolute C_2H_5OH and 5 drops of $(C_2H_5)_2O$, were cooled to 0°, then mixed in a vessel surrounded by an ice bath. After the solution was stirred for 1 min., the yellow-orange S-bonded product was precipitated by the addition of 50 ml. of ice water, isolated by filtration, washed with ice-cold C_2H_5OH and $(C_2H_5)_2O$, and dried *in vacuo* over P_2O_5 (yield 1.87 g., or 91%).

Anal. Calcd. for $PdAs_2C_{38}H_{30}N_2S_2$: C, 54.66; H, 3.62; N, 3.36. Found: C, 54.50; H, 3.80; N, 3.27. Found, after heating at 156° for 30 min., resulting in complete isomerization to the bright yellow N-bonded isomer: C, 55.01; H, 3.86; N, 3.63.

[Pd(bipy)(SCN)$_2$].—K$_2$[Pd(SCN)$_4$] (0.42 g., 1 mmole), dissolved in 10 ml. of absolute C_2H_5OH and 5 drops of H_2O, and 2,2′-bipyridine (0.16 g., 1 mmole), dissolved in 10 ml. of absolute C_2H_5OH and 5 drops of $(C_2H_5)_2O$, were cooled to −78° in a Dry Ice–acetone bath, then mixed in a vessel surrounded by a Dry Ice–acetone bath. No formation of solid took place. The solution was removed from the bath and after about 10 min. had become opaque. An unidentified orange solid was removed by filtration and the desired light orange-yellow S-bonded isomer immediately separated in the filtrate. This was isolated, washed with −78° C_2H_5OH and $(C_2H_5)_2O$, and dried *in vacuo* over Mg(ClO$_4$)$_2$.

Anal. Calcd. for $PdC_{12}H_8N_4S_2$: C, 38.04; H, 2.13; N, 14.79. Found: C, 38.17; H, 2.48; N, 14.95. Found, after heating at 156° for 30 min., resulting in complete isomerization to the light yellow N-bonded isomer: C, 38.56; H, 2.43; N, 14.81.

[Pd(bipy)$_2$][Pd(SCN)$_4$].—An acetone solution of 0.11 g. (0.25 mmole) of K$_2$[Pd(SCN)$_4$] was cooled to −78° in a Dry Ice–acetone bath. To this solution was added 0.32 g. (0.3 mmole) of [Pd(bipy)$_2$](B(C$_6$H$_5$)$_4$)$_2$. Filtration yielded a pink solid. The product, dried *in vacuo* over Mg(ClO$_4$)$_2$, contained some entrapped K[B(C$_6$H$_5$)$_4$], as determined from the infrared spectrum of the product.

Sources of Additional Compounds.—The following compounds were obtained from the indicated individuals, Chemistry Department, Northwestern University: R. C. Johnson: *cis*- and *trans*-[Pt(NH$_3$)$_2$Cl$_2$], [Pt(en)X$_2$] (en = ethylenediamine; $X^- = Cl^-$, SCN^-), [M(tripy)X]X (M = Pd(II), Pt(II); tripy = 2,2′,2″-tripyridine; $X^- = NCS^-$, Cl^-, Br^-, I^-); T. Schenach: [*trans*-Pd(P(*n*-C$_4$H$_9$)$_3$)$_2$Cl$_2$]; K. Stephen: [Pt(NH$_3$)$_4$][PtCl$_4$].

Analyses.—Platinum contents were determined gravimetrically by igniting a weighed sample of the compound in a porcelain crucible over a Meker burner. Carbon, hydrogen, and nitrogen analyses were performed by Miss H. Beck, Chemistry Department, Northwestern University.

Visible and Ultraviolet Spectra.—Visible and ultraviolet absorption spectra were measured on either a Beckman DK-2 or Cary Model 11 recording spectrophotometer. Solutions of the compounds in question in 0.1 or 1.0 cm. quartz cells were usually used, although some visible transmission spectra[17] were taken of Nujol mulls of solid samples, using quartz plates. Pieces of Whatman No. 1 filter paper, impregnated with Nujol, served as dispersing media in the sample and reference beams.

Infrared Spectra.—Infrared spectra of samples in KBr disks were measured on either a Baird-Associates Model AB-2 or Beckman IR-5 recording spectrophotometer. Both are double-beam instruments with NaCl optics. Infrared spectra of Nujol mulls of solid samples were obtained on either of the above-named instruments or on a Beckman IR-9 recording spectrophotometer, employing a KBr prism coupled with a diffraction grating. NaCl plates were used in preparing the mulls in all cases, except when the spectrum was taken on the Beckman IR-9 instrument, in which case KBr plates were used. A polystyrene standard was used for calibration in all cases. High resolution infrared spectra of Nujol mulls of solid samples in the thiocyanate C–N stretching frequency range were measured on a Perkin-Elmer Model 112 single beam recording spectrophotometer, using a CaF_2 prism and NaCl plates. The instrument was calibrated in this range on CO vapor by Dr. D. F. Shriver. Infrared solution spectra, using matched NaCl cells, were measured on a Baird-Associates Model 4-55 recording spectrophotometer.

Conductance Measurements.—Conductances of compounds dissolved in N,N-dimethylformamide (Eastman Spectro grade) at 25° were measured with an Industrial Instruments, Inc., Model RC-16 conductivity bridge and a cell with platinum electrodes.

Dipole Moment Measurements.—The dipole moments of [Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$] and [Pd(As(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$], dissolved in benzene, were determined according to the approximate method of Jensen and Nygaard,[18] using only dielectric constant measurements. The apparatus employed was a General Radio Co. Capacitance Measuring Assembly, Type 1610-A, set at 1000 c.p.s. An oscilloscope was used to balance the bridge. The capacitance measurements of the benzene solutions were made in a 40-ml. specially designed cell. Neglecting electron and atom polarizations is said to introduce an error of only a few per cent.

Rates of Isomerization.—The rate of isomerization of [Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$] to [Pd(As(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$] was studied in KBr disks by observing the decrease in intensity of the S-bonded thiocyanate C–N stretching band with time. A Perkin-Elmer Model 112 single-beam recording spectrophotometer was used. One KBr disk was used throughout an entire kinetic run. Its spectrum was measured over the 5000–650 cm.$^{-1}$ range on a Baird AB-2 double-beam recording spectrophotometer before and after the kinetic run to determine whether any decomposition of the complex had occurred. No Br^- substitution was observed. Throughout the course of the run, the disk, in a metal holder, was heated at the desired temperature in either a thermostated oven or electric coil heater. The spectra were measured *vs.* air.

For this study, the usual first-order rate expression becomes

$$k = -(2.303/t) \log (A - A_\infty) \qquad (1)$$

where k is the first-order rate constant in sec.$^{-1}$, t is the time in sec., A is the absorption at time t, and A_∞ is the absorption at infinite time. Although spectrally pure S- isomer was used in preparing the KBr disks, the high pressure and heat encountered in their preparation caused partial isomerization to the N- isomer to occur and, as a result, both C–N stretching bands were always present in the initial spectra of the disks.

The concentration of the complex is proportional to log (A −

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TABLE II

EFFECT OF OTHER LIGANDS ON THIOCYANATE BONDING.
C–S AND C–N STRETCHING FREQUENCIES OF Pd(II) AND Pt(II) THIOCYANATE COMPLEXES

Complex	C–N stretch, cm.$^{-1}$ (ν_3 SCN)	C–S stretch, cm.$^{-1}$ (ν_1 SCN)
	Thiocyanates	
$K_2[Pd(SCN)_4]$[a]	2118, 2086	703, 707 sh, 696 sh
$K_2[Pt(SCN)_4]$[a]	2120, 2089	697, 700 sh, 690 sh
$[Pd(Sb(C_6H_5)_3)_2(SCN)_2]$	(M) 2119 sh, 2115 s,sp	(D)[b]
$[Pt(Sb(C_6H_5)_3)_2(SCN)_2]$	(M) 2123 sh, 2120 s,sp	(D)[b]
$[Pd(\gamma\text{-pic})_2(SCN)_2]$	(M) 2109 s,sp	(D) 702 w
$[Pd(4\text{-}n\text{-ampy})_2(SCN)_2]$	(M) 2111 s,sp	(D) 707 w
$[Pd(phen)(SCN)_2]$	(M) 2114 s,sp	(D) 696 w
$[Pd(tu)_2(SCN)_2]$	(M) 2107 s,sp	(D) 703 w
$[Pd(etu)_2(SCN)_2]$	(M) 2101 s,sp	(D) 701 w
$[Pt(en)(SCN)_2]$	(M) 2114 s,sp	(M) 696 w
cis-$[Pt(NH_3)_2(SCN)_2]$	(M) 2116 s,sp	(M) 698 w
trans-$[Pt(NH_3)_2(SCN)_2]$	Not det.	(M) 706 w
	Isothiocyanates	
$[Pd(P(n\text{-}C_4H_9)_3)_2(NCS)_2]$	(M) 2102 s,br	(D) 847 m
$[Pd(P(C_6H_5)_3)_2(NCS)_2]$	(M) 2093 s,br	(D) 853 m
$[Pt(P(C_6H_5)_3)_2(NCS)_2]$	(M) 2097 s,br	(D) 859 m
$[Pd(As(n\text{-}C_4H_9)_3)_2(NCS)_2]$	(M) 2111 s,br	(M) 844 w
$[Pt(As(C_6H_5)_3)_2(NCS)_2]$	(M) 2090 s,br	(D) 861 m
$[Pd(py)_2(NCS)_2]$	(M) 2115 s,sp	(D) 865 w
$[Pt(py)_2(NCS)_2]$	(M) 2123 s,sp	(D) 847 w
$[Pt(bipy)(NCS)_2]$	(M) 2095 s,br	(D) 844 m
$[Pd(tripy)(NCS)_2]$[c]	(M) 2088 s,br	(D) 848 w
$[Pt(tripy)NCS]SCN$[d]	(M) 2089 s,br, 2040 s,br	(D) 863 w

[a] Frequencies taken from ref. 11. [b] No C–S stretching peak in N-bonded range; strong phenyl ring absorption in S-bonded range. [c] tripy coordinated as a bidentate ligand—no C–N stretching band found for ionic thiocyanate. [d] tripy coordinated as a tridentate ligand—ionic thiocyanate C–N stretching band at 2040 cm.$^{-1}$. Abbreviations: M, Nujol mull; D, KBr disk; s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder.

TABLE III

C–N AND C–S STRETCHING FREQUENCIES, COLORS, MELTING POINTS, MOLAR CONDUCTANCES, AND DIPOLE MOMENTS OF THIOCYANATE LINKAGE ISOMERS

Complex	Color	M.p. (dec.), °C.	C–N stretch, cm.$^{-1}$	C–S stretch, cm.$^{-1}$	Λ_m,[d] ohm^{-1} cm.$^{-2}$ mole^{-1}	Dipole moment, D.
$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	Yellow-orange	195[a]	(M) 2119 s,sp	(M)[b]	13.3	3.8
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	Bright yellow	195	(M) 2089 s,br	(M) 854 m	13.8	3.6
$[Pd(bipy)(SCN)_2]$	Light orange-yellow	270[c]	(M) 2117 m,sp, 2108 s,sp	(M) 700 w	20.3	Not det.
$[Pd(bipy)(NCS)_2]$	Light yellow	270	(M) 2100 s,br	(M) 842 m, 849 sh	20.8	Not det.

[a] Complex, upon heating, became bright yellow in color at ~130°. [b] No C–S stretching band in N-bonded range, strong phenyl ring absorption in S-bonded range. [c] Complex, upon heating, became light yellow in color at ~120°. [d] Concentration 1 m*M*. Molar conductances of approximately 70 correspond to 1:1 electrolytes, the values here are due to partial solvation (ionization) of the non-ionic complexes in DMF.

A_∞), since the cell length remains constant throughout a kinetic run. Straight lines, the slopes of which are equal to $-k/2.303$, were obtained from plots of t *vs.* log $(A - A_\infty)$. The time, t, refers to the time the disks were in the oven or heater. It was felt that, since the rates of isomerization were so slow at the temperatures employed, the isomerization reaction was effectively quenched when the disk was removed from the heat source. No serious scattering of points resulted from making this correction. It would have been desirable to study the isomerization reaction in Nujol mulls, but experimental difficulties (flowing of the Nujol layer at the temperatures employed and consequent scattering of points) prohibited this.

Results

The type of thiocyanate bonding in the thiocyanate-containing complexes was determined on the basis of the position of the thiocyanate C–S stretching frequency for the complex in question. As has been pointed out by several authors,[11,19] this frequency is shifted to higher wave numbers in the spectra of isothiocyanates, and to lower wave numbers in the spectra of thiocyanates, both relative to the C–S stretching frequency of "ionic" thiocyanate, as in KSCN (749 cm.$^{-1}$).[20] Turco and Pecile[11] give the following ranges: M–SCN, 690–720 cm.$^{-1}$; M–NCS, 780–860 cm.$^{-1}$. The position of the C–S stretching frequency in each case was determined by comparing

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(19) (a) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959); (b) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961); (c) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 175.

(20) L. H. Jones, *J. Chem. Phys.*, **25**, 1069 (1956).

the spectrum of the thiocyanate-containing complex with that of the analogous chloro complex. The C–N and C–S stretching frequencies found for the complexes are listed in Table II.

The C–N and C–S stretching frequencies of the two linkage isomeric pairs and other pertinent data concerning them are shown in Table III.

The absorption maxima found in the visible and near-ultraviolet spectra of $[Pd(As(C_6H_5)_3)_2(SCN)_2]$ and $[Pd(As(C_6H_5)_3)_2(NCS)_2]$, as well as those found in the spectra of other complexes germane to the discussion which follows, are shown in Table IV.

TABLE IV

VISIBLE AND NEAR-ULTRAVIOLET SPECTRA

Complex	Solvent	Absorption, maxima, 700–350 mμ ($\epsilon \times 10^{-4}$)
$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	$HCCl_3$	351 (2.09)[a]
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	$HCCl_3$	351 (2.09)
$[Pd(As(C_6H_5)_3)_2(SCN)_2]$	Nujol mull	395, 475 sh
$[Pd(As(C_6H_5)_3)_2(NCS)_2]$	Nujol mull	350
$K_2[PdCl_4]$	Nujol mull	475
$[Pd(bipy)_2][PdCl_4]$	Nujol mull	475
$K_2[Pd(SCN)_4]$	Nujol mull	500 (sh), 410 (sh)
$[Pd(bipy)_2][Pd(SCN)_4]$	Nujol mull	500 (sh), 410 (sh)

[a] $[Pd(As(C_6H_5)_3)_2(SCN)_2]$ evidently isomerizes to the stable N- isomer upon dissolution in $HCCl_3$ at room temperature.

The rate constants determined for the isomerization of $[Pd(As(C_6H_5)_3)_2(SCN)_2]$ in KBr disks at 126 and 147° were, respectively, 3.47×10^{-5} and 7.81×10^{-5} sec.$^{-1}$. Qualitatively, it was observed that, in the pure solid state, complete isomerization took place in less than 2 hr. at 118°.

Discussion

Turco and Pecile[11] suggest that π-bonding ligands, such as phosphines, coordinated to Pd(II) or Pt(II) enhance M–NCS bonding in these four-coordinated systems. They point out that there are two sets of antibonding π-orbitals localized on the sulfur atom, which, along with the sulfur atom's vacant d-orbitals, can accept electron density from the metal's filled nonbonding d-orbitals, resulting in additional stability of the M–S bond. The importance of this additional stability will depend on the availability of the electrons of the metal and their relative energy as compared with that of the orbitals of the thiocyanate. Strong π-electron acceptors, as trialkylphosphines are believed to be,[21] can make the metal d-orbital electrons less available for donation to the thiocyanate, removing the source of additional stability for the M–S bond.

Another way of saying about the same thing is that π-bonding ligands in these systems tend to reduce the electron density on the metal and thereby change class b, or soft metals, to class a, or hard metals. This is accompanied by a change in M–SCN bonding to M–NCS, respectively. Such a π-bonding hypothesis finds support in the observation (Table II) that the bonding is Pd–NCS in the pyridine complex, but Pd–SCN in the analogous γ-picoline and 4-*n*-amylpyridine complexes. Alkyl substitution donates electron density into the pyridine ring, opposing the withdrawal of d-electron density by the ring from the Pd(II), relative to pyridine. The greater σ-bonding of the more basic alkylpyridines may also increase the electron density on Pd(II), relative to pyridine, and further promote Pd–SCN bonding. It is important to note that, in these systems, the steric factors at the metal are kept constant. This then shows that the electronic factors of coordinated ligands can alter the nature of SCN^- bonding in metal complexes. It also suggests that small differences can sometimes change the type of bonding.

It has been shown recently[22] that steric factors can alter the nature of SCN^- bonding in these systems. In most comparisons, such as $[Pt(NH_3)_2(SCN)_2]$ and $[Pt(PR_3)_2(NCS)_2]$, both electronic and steric factors change with changes in the ligands. It is then often impossible to assess the importance of each factor to the type of SCN^- bonding. The point is that M–SCN bonding, because of the angular structure of M–S–C, has a larger steric requirement than does the linear structure of M–NCS.[23] Thus, because of the larger size of PR_3, it would tend to generate some strain in M–SCN and promote M–NCS bonding. The steric factor of PR_3 operates in the same direction as does its electronic effect, and both may well contribute. Similarly, the difference found between $P(C_6H_5)_3$ and $Sb(C_6H_5)_3$ may be the result of electronic and/or steric factors. This is because $P(C_6H_5)_3$ is the better π-bonder[24] and, because of the smaller size of phosphorus, it places the phenyl groups nearer to the metal and offers a greater steric hindrance at the metal than does $Sb(C_6H_5)_3$. That 1,10-phenanthroline and 2,2′-bipyridine cause different types of SCN^- bonding is not understood, except to repeat that small differences are sufficient to cause a change in bond type.

In all of these systems the type of bonding, M–NCS or M–SCN, was assigned on the basis of the infrared spectra in the C–S stretching region.[11,19] In most cases, the thiocyanato complexes exhibited very sharp well-formed C–N stretching peaks above 2100 cm.$^{-1}$, whereas the isothiocyanato complexes exhibited relatively broad, more intense peaks around or below 2100 cm.$^{-1}$. The apparent exceptions, where the positions of the C–S stretching frequencies support N-bonding, are $[Pt(py)_2(NCS)_2]$, $[Pd(py)_2(NCS)_2]$, and $[Pd(As(n\text{-}C_4H_9)_3)_2(NCS)_2]$. Most of the thiocyanato complexes which were thought to have the *cis* configuration exhibited an expected splitting of the C–N stretching band, the exceptions being $[Pt(en)(SCN)_2]$ and $[Pd(phen)(SCN)_2]$. None of the *cis*-isothiocyanato complexes exhibited this splitting.

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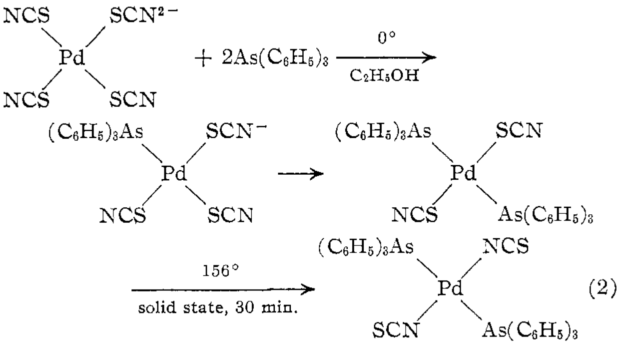
(21) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959); W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 123 (1963).

(22) F. Basolo, W. H. Baddley, and J. L. Burmeister, *ibid.*, **3**, 1202 (1964).

(23) See discussion and references in ref. 20b. It should be noted that in the solid state, some M–NCS systems are angular, with large angles of about 160°.

(24) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

Having observed that $As(C_6H_5)_3$ is a borderline ligand between $P(C_6H_5)_3$, which gives Pd–NCS, and $Sb(C_6H_5)_3$, which gives Pd–SCN, it was decided to use $As(C_6H_5)_3$ to prepare the first example of linkage isomers in these systems. This was achieved by the reaction shown in eq. 2.


(2)

The experiment was designed such that the S-bonded kinetic product could be isolated prior to its rearrangement to the more stable N-bonded isomer. This required that the reaction be carried out at some low temperature under conditions such that the product could be separated rapidly from the reaction mixture. Thus, a nonionic complex of slight solubility was prepared. Pd(II), rather than Pt(II), was used because the substitution reactions of Pd(II) are much more rapid than those of Pt(II). The infrared spectrum of the yellow-orange product obtained under these conditions showed the complete absence of the N-bonded C–S stretching peak at 854 cm.$^{-1}$, and, as predicted by Mitchell and Williams,[7] the C–N stretching peak was found at a higher frequency, 2119 cm.$^{-1}$, than that (2089 cm.$^{-1}$) of the N-isomer. Heating the S- isomer at 156° for 30 min. resulted in complete isomerization to the bright yellow N- isomer. It was then determined, by the use of high resolution infrared spectroscopy in the C–N stretching frequency range, that what results from the reaction at room temperature is actually a mixture of the two isomers.

In *ca.* 10^{-4} *M* chloroform solution, the visible–near-ultraviolet spectra of the two isomers are identical (see Table IV), indicating rapid isomerization to the same equilibrium mixture upon dissolution. The visible transmission spectra of Nujol mulls of the isomers are quite different, however (Table IV). The band corresponding to the d–d transition of the N- isomer is apparently hidden by its charge-transfer band at 351 mμ; that of the S- isomer is seen as a shoulder at 475 mμ.

In an attempt to obtain some information concerning the structure (*cis* or *trans*) of these linkage isomers, the dipole moments of both were determined in benzene solution. The results were inconclusive. The dipole moment of the S- isomer was found to be 3.8 D., that of the N- isomer 3.6 D. That both are the same, within the limits of experimental error, is without meaning because the infrared spectra of the two solutions are identical. This suggests again that there is rapid equilibration upon dissolution at room temperature. The solutions exhibit three C–N stretching peaks: ~2090, ~2120, and ~2160 cm.$^{-1}$. The high frequency of the peak at 2160 cm.$^{-1}$ indicates that thiocyanate bridging[5] takes place in solution. Thus, there is no evidence concerning the geometric structures of the linkage isomers, and the arbitrary choice of *trans* for both is made on the basis that, for steric reasons, the bulky $As(C_6H_5)_3$ groups would prefer to be at opposite positions in the complex. Support for this choice is found in the previously cited work of Mann and Purdie.[13]

Consequently, to obviate the possibility of concurrent geometric isomerism, a bidentate ligand, 2,2′-bipyridine, was employed in a manner similar to that used in preparing the triphenylarsine derivatives. Isolation of the light orange-yellow S- isomer, $[Pd(bipy)(SCN)_2]$, was accomplished by lowering the temperature of the reaction to −78° (the temperature of a Dry Ice–acetone bath). Complete isomerization to the light yellow N-bonded isomer, obtained from the room temperature reaction, was accomplished by heating the S- isomer at 156° for 30 min. The only other reasonable compound which would give the same analytical results as the S-bonded isomer is $[Pd(bipy)_2][Pd(SCN)_4]$. Although the conductivity measurements (Table III) seem to rule out this possibility, it was felt that the most convincing evidence would be gained by actually preparing this Magnus type complex. Its visible transmission spectrum (Nujol mull) exhibits shoulders at 500 and 410 mμ which are also found in the spectrum of $K_2[Pd(SCN)_4]$ (Table IV), but are absent in the spectrum of $[Pd(bipy)(SCN)_2]$ and $[Pd(bipy)(NCS)_2]$, neither of which shows any absorption maxima in the visible range.

A comparison of the rates of isomerization of solid $[Pd(As(C_6H_5)_3)_2(SCN)_2]$ in KBr disks with qualitative observations of the rate of isomerization in the pure solid state shows that a large decrease in rate results from carrying out the isomerization in a KBr disk. It is of interest to note that the isomerization, nitrito → nitro, shows no difference in rate when carried out in a KBr disk.[3] It would, of course, have been desirable to investigate the rates and mechanism of isomerization in solution, but the isomerization in the solvents used was too fast to permit such a study by conventional techniques.

In conclusion, it should be mentioned that other examples of M–SCN and M–NCS linkage isomers have recently been reported. Zinc(II) forms Zn–NCS and mercury(II) forms Hg–SCN bonded complexes; cadmium(II) is intermediate in character in that both Cd–SCN and Cd–NCS bonded species have been observed in solution. This was first reported by Tramer[25] on the basis of infrared and Raman spectral studies. Plane[26] has made similar observations using Raman spectra. Similar results were recently re-

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[25] A. Tramer, *J. chim. Phys.*, **59**, 232 (1962); "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, New York, N. Y., 1964, p. 225.

[26] R. A. Plane, private communication.

ported[27] on the basis of n.m.r. investigations. Finally, Wojcicki and Farona[28] have just reported the isolation of the linkage isomers [$Mn(CO)_5SCN$] and [$Mn(CO)_5NCS$].

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(27) O. W. Howarth, R. E. Richards, and L. M. Venanzi, in press.

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Free Energies of Some Heavy-Metal Ferrocyanides[1]

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The free energies of formation (kcal.) of the following ferrocyanides from their ions at 25° have been determined by e.m.f. measurement using cells without liquid junctions: $Pb_2Fe(CN)_6$, −24.58; $Ag_4Fe(CN)_6$, −60.11; $Cd_2Fe(CN)_6$, −23.70; $K_2CdFe(CN)_6$, −23.32; $Zn_2Fe(CN)_6$, −21.40; $KZn_{1.5}Fe(CN)_6$, −28.77; $K_2Cu_2Fe(CN)_6$, −36.36; *i.e.*, the reported free energy change refers, *e.g.*, to the reaction

$$2K^+(aq, a = 1) + Cd^{2+}(aq, a = 1) + Fe(CN)_6^{4-}(aq, a = 1) = K_2CdFe(CN)_6(s)$$

X-Ray diffraction data, taken from powder patterns run on analyzed samples, for several metal ferrocyanide salts are also reported.

There are few thermodynamic data on heavy-metal ferrocyanides,[2–4] perhaps because experimental thermodynamicists do not like to work with solids that tend to be colloidal.[5] We report here a method for preparing them in high purity and noncolloidal form, and the free energies of a number of them at 25° from e.m.f. measurements.

Experimental

Reagents.—Solutions were made from reagent grade chemicals and nitrogen-saturated water. Lead, cadmium, and zinc amalgams were made from reagent grade metals and triple-distilled mercury, and just before use were washed with 6 *M* HNO_3 and distilled water. Potassium amalgam was made by electrolysis of 2 *M* KOH with a platinum anode and mercury cathode, dried on the vacuum line, and transferred under dry nitrogen. Tetraethylammonium ferrocyanide solution was prepared by neutralizing tetraethylammonium hydroxide with freshly prepared (*vide infra*) ferrocyanic acid solution. Reagent grade $K_4Fe(CN)_6 \cdot 3H_2O$ was recrystallized from nitrogen-saturated distilled water below 60° and stored in a darkened desiccator over saturated aqueous $NaBr \cdot 2H_2O$.

Synthesis of Ferrocyanides.—The following procedure served for preparing $Cu_2Fe(CN)_6$, $Zn_2Fe(CN)_6$, and $Cd_2Fe(CN)_6$: A column of cation-exchange resin, Dowex AG-50W-X8, was prepared in the hydrogen ion form. A 0.5 *M* solution of $K_4Fe(CN)_6$ was poured onto the column and the effluent $H_4Fe(CN)_6$ run directly into a stirred twofold excess of 0.8 *M* cupric, zinc, or cadmium acetate solution. After stirring for 1 hr. at room temperature the precipitate was washed by repeated decantation (about 15 washings) until the wash water gave no test for metal ion.

We prefer the ion-exchange method for making ferrocyanic acid to the ether adduct method described by Weiser and coworkers,[5] since solid ferrocyanic acid is rather susceptible to decomposition on storage. The acetate salt is used in this synthesis so that its buffer action can prevent the buildup of hydrogen ion, which if present makes the precipitate more colloidal and at high concentration can even incorporate in the crystal.

Samples of $Pb_2Fe(CN)_6$ and $Ag_4Fe(CN)_6$ were prepared by simply mixing solutions of the corresponding soluble salts, since they do not precipitate as colloids or incorporate alkali in the crystals.[6–8]

Cuprous ferrocyanides were prepared by making cupric sulfate solution ammoniacal, reducing it with hydroxylamine sulfate, then adding potassium ferrocyanide. We did not make use of the solid resulting when cuprous was in excess, which was pale green (possibly $[Cu(NH_3)_2]_4Fe(CN)_6$) but turned white on treatment with dilute sulfuric acid, had a $Cu:Fe(CN)_6$ ratio of 4.08 ± 0.05, and was presumably $Cu_4Fe(CN)_6$. The solid we used in our measurements was precipitated when $K_4Fe(CN)_6$ was in excess, was white, and analysis showed it to have a $Cu:Fe(CN)_6$ ratio of 2.00 ± 0.01, corresponding to $K_2Cu_2Fe(CN)_6$.

A sample of $K_2CdFe(CN)_6$ was made by preparing dilute (0.01 *M*) $CdSO_4$ solution, almost saturated with KNO_3, and adding to it an equal volume of almost saturated $K_4Fe(CN)_6$. The same procedure was followed in an attempt to prepare the corresponding zinc salt, as reported by Rigamonti.[9] However, the product was always the sesquizinc ferrocyanide, $KZn_{1.5}Fe(CN)_6$, the same product produced by mixing stoichiometric amounts of the zinc and ferrocyanide reagents, as indicated by analysis and X-ray pattern.

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(1) This work constitutes part of the Ph.D. thesis of Peter A. Rock, University of California, Berkeley, 1964.

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(3) J. N. Pearce and L. D. Ough, *J. Am. Chem. Soc.*, **60**, 80 (1938).

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(6) H. T. S. Britton and E. N. Dodd, *J. Chem. Soc.*, 1543 (1933).

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(9) R. Rigamonti, *Gazz. chim. ital.*, **68**, 803 (1938).